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ON THE PHOSPHORESCENCE OF ZnS-Cu-Sm

- COMMUNIST CHINA -

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FOREWORD

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EFFECT OF INFRARED IRRADIATION DURING EXCITATION

ON THE PHOSPHORESCENCE OF ZnS-Cu-Sm

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Following is a translation of an article by Hsu Ju-chun (6079,3067,6874), Wang Jui-min (3769,3843,3046), Chung Ko-i (6945,2706,0308), and Huang Mei-jung (7806,5019,1369) in the Chinese-language periodical Wu-li Hsueh-pao (Acta Physica Sinica), Peiping, Vol XV, No 10, 6 October 1959, pages 550-557.

Abstract

In this article, the effect of the intensity of excitation and the infrared irradiation during excitation on the decay time constant τ and intensity J of phosphorescence of ZnS-Cu-Sm was studied. The changes of τ and J under different conditions of excitation by the sun were compared. With the help of the measurement of radiation as a function of increasing temperature, we found the mechanism responsible for the change of phosphorescence by infrared irradiation during excitation.

Some phorescent materials continue to emit light after ultraviolet irradiation. This is called phosphorescence. Materials with long periods of phosphorescence is commonly called permanent phorescent materials. They are ideal phorescent materials. They can be used for low-intensity lighting purposes. Since these materials do not need repeated excitation, they can be very conveniently used. With a few minutes excitation by sun or lamp light, these materials should continuously emit light for many minutes, or even many hours. Therefore, they have great economical value.

During the period of phosphorescence, one demands high light intensity and long duration. The decay of intensity as a function of time can be approximated by $J = A e^{-t/\tau}$. Therefore we use τ as an indication of the decay rate. Small τ means slow decay, while large τ means rapid decay and short period of phosphorescence.

ZnS-Cu-Sm is a permanent phorescent material. It emits light for a long period of time after irradiation by sun lamp, sunlight, daylight lamp or ultraviolet radiation. It possesses the advantages of the common phorescent powder. However, J and τ for this material

depends on the nature of excitation; they have different values according to whether the excitation is by sunlight or ultra-violet radiation. The understanding of the reasons behind this effect should prove very useful in the future in utilizing these materials.

1. Results of Initial Experiment

In preparing ZnS-Cu-Sm, we have changed the concentration of Cu and Sm, the kinds of catalyst and the temperature and pressure during heating. After irradiation by sunlight and ultraviolet radiation (π PK2 mercury lamp and UG-5 filter were used), the values of J and ϕ were compared. The results are shown in the following table and figure 1 and 2. The plot is on a logarithmic scale.

It can be seen from the results that the phosphorescent intensity of ZnS-Cu-Sm after 5 minutes irradiation by sunlight is weaker than that caused by ultraviolet irradiation. Moreover, the rate of decay is also different for these two cases. In a few cases, the ϕ values for these two cases are very close, or the sunlight excitation gives higher value of ϕ . However in the majority of the cases, ϕ has a smaller value when excited by sunlight. Most notable cases were material No. 249 ($1.36 \rightarrow 1.22$) and No. 324. The changes in these 2 materials were most pronounced.

We considered the causes for this effect. They could be (1) the intensity of excitation radiation is different for the case of sunlight and ultraviolet radiation (2) the contamination of sunlight by the infrared. To understand these causes, we irradiate ZnS-CuSm with infrared after excitation by ultraviolet radiation. We discovered that it blinks after this treatment.

Next we compared the intensity of phosphorescence after irradiation by sunlight and ultraviolet radiation from a mercury lamp. We used UG-5 filter to filter out the visible light. The time of irradiation for both cases is five minutes. The intensity of phosphorescence is plotted in figure 3. The results show that the phosphorescent intensity after excitation by π PK-2 mercury lamp is 1.8 times that excited by sunlight, (the relative intensity 200 seconds after irradiation). Therefore we conclude that both the infrared radiation and the intensity of excitation radiation affect the phosphorescence of ZnS-Cu-Sm. We analyzed the basic mechanism for these effects in the following sections.

Material No.	α_1	α_2	J ₁	J ₂	Material No.	α_1	α_2	J ₁	J ₂
836	1.20	1.26	1900	2300	244	1.30	1.37	620	470
136	1.50	1.42	2000	2000	132	1.39	1.39	2100	2100
137	1.36	1.45	1650	1900	133	1.30	1.36	2300	2350
670	1.27	1.32	2900	3900	134	1.34	1.43	2600	2600
672	1.20	1.28	1600	1700	246	1.50	1.56	350	600
683	1.37	1.36	1300	1500	247	0.87	0.88	760	1300
593	1.27	1.31	850	1000	248	0.83	0.89	450	1050
594	1.29	1.30	800	1000	249	1.22	1.36	1600	2350
597	1.32	1.29	2600	2200	987	1.47	1.45	3300	3500
598	1.33	1.40	3200	3500	828	1.29	1.29	1300	1800
539	1.23	1.28	420	1080	829	1.12	1.20	900	1000
540	1.24	1.25	510	900	830	1.30	1.22	2100	2900
541	1.24	1.26	750	620	831	1.25	1.26	850	1000
542	1.19	1.27	550	800	832	1.19	1.22	550	880
324	1.32	1.40	460	1250	834	1.27	1.29	1800	1900
325	1.28	1.33	1000	1500	835	1.20	1.24	900	750
326	1.33	1.32	1500	1800					

- Explanation:
1. J₁ is the intensity of phosphorescence after sunlight excitation in relative units (photo-electric current 200 seconds after excitation); J₂ is the intensity of phosphorescence after ultra-violet excitation in relative units (photo-electric current 200 seconds after excitation); α_1 is the decay time constant after sunlight excitation; α_2 is the decay time constant after ultra-violet excitation.
 2. Time of sunlight excitation is 10 minutes
 3. Ultraviolet source is π PK-2 mercury lamp after filtration by UG-5 filter. The time of ultraviolet excitation is 2 minutes.

2. The Effect of Infrared Irradiation

The infrared source used in 220V-200W tungsten lamp. The light is filtered by RG-7 filter to eliminate the visible light. The transmitted light has a wave length from 8000 \AA up. The maximum intensity lies around 1.2 μ .

(1) Does infrared radiation cause sudden recovery or blinking action? What is its effect on J?

After infrared irradiation of ZnS-Cu-Sm during its excitation, one observes some blinking light after which the intensity of light diminishes gradually. From the heat-induced light intensity (see figure 4) of samples irradiated by both infrared and ultraviolet radiation and by ultraviolet radiation alone, one sees that the first-mentioned process gives much less intensity. Thus, one can see that infrared radiation does affect the phorescence of ZnS-Cu-Sm.

From the heat-induced light intensity of ZnS-Cu-Sm one can see the following: by comparing the total light intensity (heat-induced light plus blinking light) of infrared irradiation ZnS-Cu-Sm during ultra-violet excitation with the heat-induced light intensity of ZnS-Cu-Sm without infrared radiation, one can judge the effect of the infrared irradiation.

The curve a of figure 5 is obtained by irradiating ZnS-Cu-Sm with ultraviolet for 5 minutes, and then increasing the temperature from room temperature at constant rate. Curve b is obtained by infrared irradiation for 10 seconds after the five-minute ultraviolet irradiation. The blinking light was instantly recorded, and then immediately afterwards the temperature was increased to obtain the heat-induced light intensity curve. From the above figure one can clearly see that the produced blinking light is very weak, it rises briefly and then decreases.

In comparing the areas under curves a and b, i.e., their total heat-induced light intensity, the total light intensity of blinking light plus heat-induced light of the infrared irradiated sample is about $\frac{1}{2}$ as much as that without infrared irradiation.

Infrared irradiation limits the accumulation of radiation and therefore decreases the intensity of phosphorescence of ZnS-Cu-Sm. From figure 3 one can see that the simultaneous excitation by both the infrared and ultraviolet radiation decreases the intensity of phosphorescence. This agrees with the work of V. L. Lenshin and V. V. Antonov - Romanovskii.

(2) The Effect of Infrared Irradiation on the Decay Time Constant τ .

After ultraviolet excitation of ZnS-Cu-Sm, we irradiate it with infrared radiation for fixed periods of time during different stages of phosphorescence and observe the effect of infrared radiation on the light intensity given out by ZnS-Cu-Sm (see Figure 6). The following table shows the measured numerical result.

From the curves b, c, of figure 6, one can see the effect of infrared radiation on ZnS-Cu-Sm; its effect on a blinking light is small. The first second of infrared irradiation produces a strong blinking light, but decreases rapidly during the 2nd second. This agrees well with the results obtained from the heat-induced light intensity.

Material No. Time When Infrared Irradiation Starts (after excitation stops) Time of Infrared Irradiation Decay Time Constant After Normal Phosphorescence Recovers

No. 324		without excitation	1.0
	3 min.	10 sec.	0.69
	5 min.	10 sec.	0.91
	10 min.	10 sec.	0.95
	10 min.	15 sec.	0.78
	15 min.	10 sec.	1.00

No. 249		without excitation	1.36
	3 min.	15 sec.	1.24
	5 min.	15 sec.	1.18
	15 min.	15 sec.	1.35

Infrared radiation during different stages of the decay of light intensity does not change the basic nature of decay rate, i.e., the decay curve being still hyperbolic. But from figure 6 and the numbers of the above table, one can see infrared irradiation during different stages of phosphorescence for fixed periods of time changes the decay time constant after recovery from the infrared irradiation. This change is regular; the longer the time between excitation and infrared irradiation the less the effect of the infrared irradiation. If this period is 15 minutes, the infrared irradiation does not cause any change of the decay time constant. However, if the duration of infrared irradiation is increased, the effect becomes more pronounced. For example, when infrared irradiated was 10 seconds in sample No. 324, 10 minutes after excitation has $\eta = 0.95$; 15 seconds infrared irradiation gives $\eta = 0.78$.

We believe these changes of the decay rates of light are caused by the fact that ZnS-Cu-Sm has different levels of metastable states. The distribution of electrons in different states has a significant effect on the rate of decay. During the initial stage of phosphorescence the infrared irradiation has a greater effect, this may be due to the fact that more electrons are in the upper state in the initial stage and infrared irradiation liberates these electrons. This greatly causes the change of distribution of electrons in the upper and lower states; therefore it affects the decay time constant. During later stages of phosphorescence most electrons are in the lower state and infrared irradiation affects these electrons very little. Therefore, it has little effect on the distribution of electrons and changes very little the decay time constant.

(3) The effect of Infrared Irradiation on the Distribution of Electrons and Its Subsequent Effect on the Heat vs. Intensity Curve

To understand the structure of the metastable states of ZnS-Cu-Sm, and the distribution of electrons after excitation, as well as to understand whether infrared irradiation causes changes of electron distribution, we measured the heating vs. light intensity curve. We irradiate ZnS-Cu-Sm for different periods of time after ultraviolet excitation and measured its heating vs. light intensity curve. Then we measured the heating vs. light intensity curve without infrared irradiation. By comparing these two curves we can see the effect on the electron distribution.

During the experiment measuring the heating vs. light intensity curve, the samples are heated from room temperature 30°C to 200°C at the rate of 20°C/min. The times of infrared irradiation are 10 seconds, 30 seconds and 5 minutes.

From the measured results one sees that curve a (with only ultraviolet excitation) has its peak between 80°C and 100°C and it is flat. This could be the superposition of several peaks. After infrared irradiation for fixed periods of time, the effect shows up on curves b, c, and d. The shape of the peak has changed; two peaks begin to appear. Therefore, we can conclude there are at least two different levels of metastable states.

From the above result one can also see that different periods of infrared irradiation (10 seconds, 30 seconds and 5 minutes) changes the peak value on the heating vs. light intensity curve. The longer-period infrared irradiation affects more the lower-temperature peak, while the effect on the higher-temperature peak is less. This shows the infrared irradiation on the different metastable states of this material is different. Infrared radiation causes the loss of electrons of the upper state more rapidly, and it causes the smaller loss of electrons of the lower state. Therefore, there are two peaks on the heating vs. light intensity curve.

Because of the process of recapture of electrons, even if infrared radiation has the same effect on the two states, when the total light intensity changes little, the change of the two peaks on the heatings vs. light intensity curve are different. But this is only pronounced when there are small number of electrons in a state. Therefore, the pronounced effect noted here has nothing to do with the recovery effect caused by electron recapture.

From the effect of infrared irradiation on the heating vs. light intensity curve we have proved that the change of the nature of phosphorescence caused by infrared radiation is due to the change of distribution of electrons in ZnS-Cu·Sm. During the initial stage of decay the number of electrons in the upper state is relatively large, and the infrared radiation has a great effect on the upper state electrons. Hence, it changes the decay time constant.

(3) The Effect of the Excitation Light Intensity

To understand the effect of the excitation light intensity on ϕ and J, we used copper wire mesh of different transparency to weaken the ultraviolet radiation intensity. We also excited ZnS-Cu·Sm with sunlight during different times of the day.

The ultraviolet source is X PK-2 mercury lamp with UG-5 filter. The copper wire mesh used is capable of weakening the light intensity 30 % and 47 %. Samples are irradiated for 5 minutes both with and without the copper wire mesh, then the decay rate and intensity of light are measured, (numbers are recorded 200 seconds after excitation).

1. Unattenuated excitation light $\phi = 1.36$ J = 1600
2. 30 % attenuation of excitation light $\phi = 1.26$ J = 920
3. 47 % attenuation of excitation light $\phi = 1.00$ J = 300

The sunlight used for excitation are at noon (clear day 12:00 noon), afternoon (4 - 5 o'clock) and at noon on a cloudy day. After ten minutes' excitation, the decay rate and intensity are measured (numbers are recorded 200 seconds after excitation).

Noon (clear day)	$\phi = 0.83$	J = 400
Afternoon (clear day)	$\phi = 0.85$	J = 620
Noon (cloudy day)	$\phi = 0.95$	J = 560

From the above numerical results one can see that the intensity of excitation does affect the phosphorescence of ZnS-Cu·Sm. When ultraviolet is used as an excitation source, the decrease of intensity changes the rate of decay from $1.36 \rightarrow 1.26 \rightarrow 1.00$; the relative strength of

phosphorescence decreases. This means when the excitation intensity is increased, the intensity of phosphorescence increases and its decay rate also increases. When sunlight is used as an excitation source, the light is not pure ultraviolet but mixed with infrared as well. Although the light intensity is strongest at noon on a clear day, the intensity of infrared is also at its strongest. Therefore, neither the decay rate nor the intensity is largest at that time. On a cloudy day the infrared intensity is small, therefore, decay time constant $\varphi = 0.95$.

V. V. Antonov-Romanovskii measured the phosphorescence of ZnS-Cu crystal under different intensities of the excitation light. He discovered that the stronger the excitation intensity, the earlier the linear relationship between $\log. J$ and $\log. t$ begins. During his measurement of sulfurous phorescent material, he obtained similar results. It seems at that time he did not investigate the effect of intensity of light on the light decay rate.

In light of the present paper, the intensity of excitation light affects the φ and J of phosphorescence. Therefore, one of the reasons why the nature of phosphorescence differs according to the excitation light (sun or ultraviolet) is that their intensities are different.

4. The Effect of Simultaneous Excitation by Ultraviolet and Infrared Light on J and φ .

Infrared light can cause the sudden recovery and diminish the light of ZnS-Cu·Sm. The intensity of excitation light also affects the phorescence of this material. Upon examination, these two effects of the phosphorescence of ZnS-Cu·Sm have important meaning.

The source of ultra-violet light used is the same as before. The infrared source is 200 W tungsten lamp with RG-7 filter. When comparing the excitation with ultraviolet light alone and that with ultraviolet and infrared simultaneously, the resultant J and φ do not show noticeable change.

Ultraviolet Excitation for 5 minutes $\varphi = 1.37$ $J = 1600$

Ultraviolet and Infrared Excitation for 5 minutes $\varphi = 1.39$
 $J = 1600$

However, if we change the intensity of ultraviolet light and keep the same infrared intensity, we discover that the rate of decay of phosphorescence changes noticeably.

47 % Attenuation of Ultraviolet light $\varphi = 1.00$ $J = 300$

47 % Attenuation of Ultraviolet light plus infrared excitation
 $\varphi = .82$ $J = 65$

From the above experiment, one can see that the effect of infrared light depends on the intensity of ultraviolet light. Under strong ultraviolet excitation, the addition of infrared excitation affects the intensity of phosphorescence, but not the rate of decay of intensity. Under weak ultraviolet excitation, the effect of infrared irradiation on the intensity is very great, hence it also causes a change in the rate of decay of phosphorescence. From the measurements on another sample, we see the effect of decreasing the ultraviolet intensity on the rate of decay of phosphorescence is very pronounced.

Under strong ultraviolet excitation, the unnoticeable effect of infrared on the decay rate of phosphorescence could be attributed to the weakness of infrared intensity. If the intensity of infrared irradiation could be increased, its effect could be observed.

Now we can understand the excitation of ZnS-Cu-Sm by sunlight, and why the nature of phosphorescence differs with the case of ultraviolet excitation. It corresponds to the case of ultraviolet excitation plus strong infrared irradiation at the same time.

Type of excitation	Decay Time Constant After 30% Attenuation of Excitation Light	Decay Time Constant After 47% Attenuation of Excitation Light
ultraviolet light	$\alpha = 1.24$	$\alpha = 0.72$
ultraviolet light + infrared light	$\alpha = 1.1$	$\alpha = 0.6$

5. Conclusions

Infrared irradiation causes a sudden recovery of excited ZnS-Cu·Sm (it also includes the appearance of a blinking light). ZnS-Cu·Sm has at least 2 levels of metastable states. Infrared radiation affects greatly the electrons in upper level, because it changes the distribution of electrons in the metastable states; hence the rate of decay of phosphorescence also changes.

On the other hand, the intensity of excitation also causes changes in J and η . However, under sunlight excitation, the change of phosphorescence is not only caused by the weakness of ultraviolet light but also by the effect of infrared light.

When utilizing sunlight for excitation of ZnS-Cu·Sm, the effect of infrared light decreases the stored light intensity, however, it also decreases the rate of decay.

The effect of infrared light on these materials could be used for many special needs.

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Figure Appendix

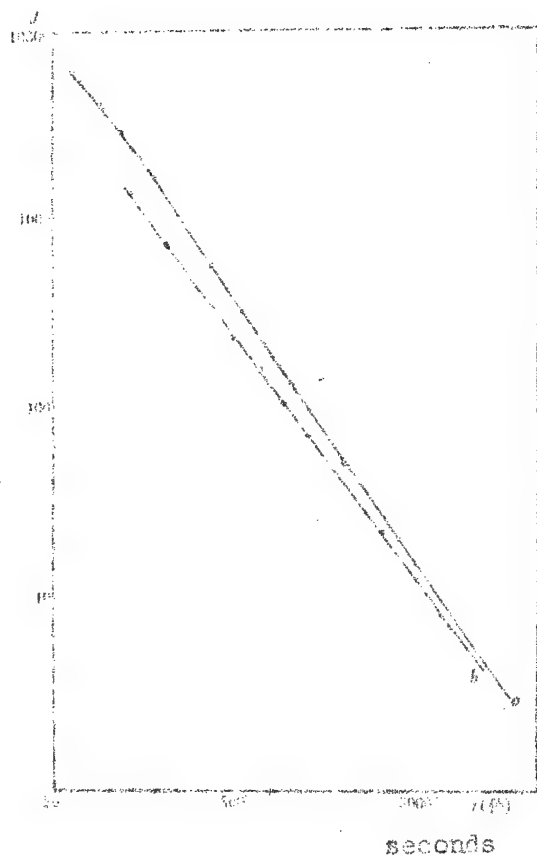


Figure 1 ZnS-Cu-Sm (No. 249 material)

The decay curve of phosphorescence after different sources of excitation

Curve a--Ultraviolet excitation (from mercury lamp) for 2 minutes

Curve b--Sunlight excitation for 5 minutes

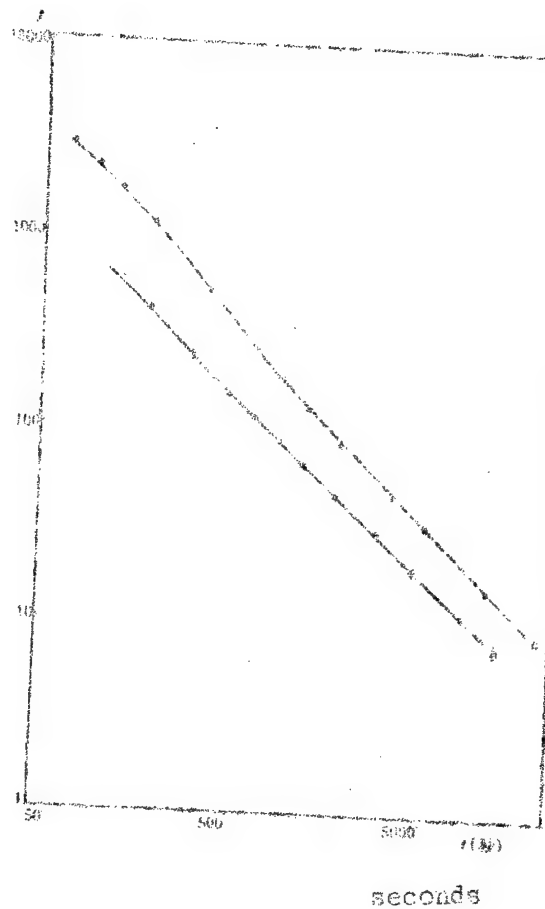


Figure 2 (same as Figure 1) ZnS-Cu-Sm No. 324

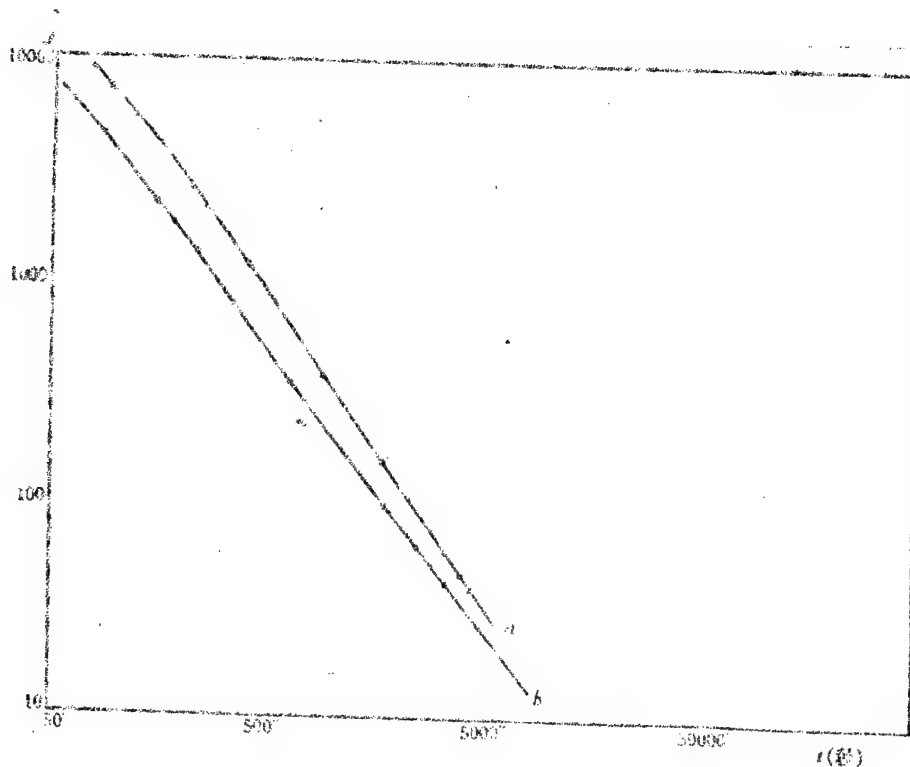


Figure 3 The comparison of the decay of phosphorescence of ZnS-Cu-Sm after ultraviolet excitation from sunlight and mercury lamp. UC-5 filter was used and the time of excitation is the same for both cases (5 minutes).
 Curve a--After mercury lamp excitation
 Curve b--After sun light excitation

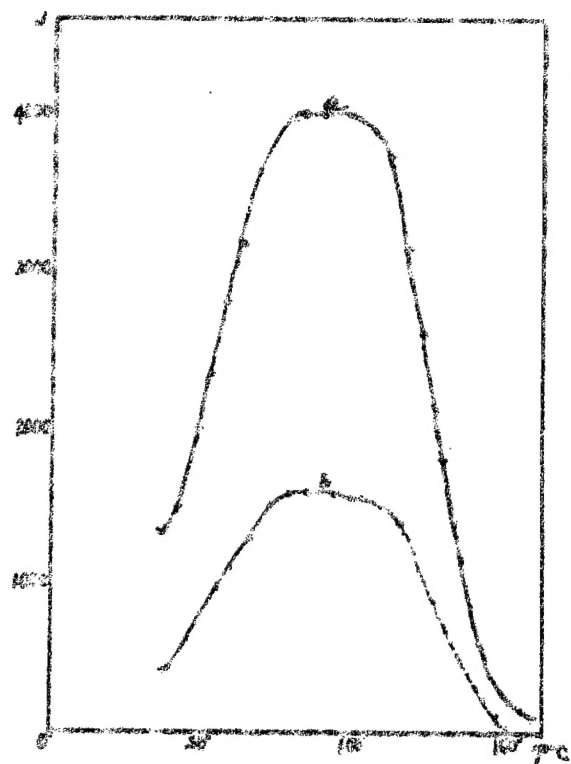


Figure 4 The Heat-Induced Light Curve of ZnS-Cu-Sm
 Curve a--Excitation by ultraviolet light from mercury lamp
 Curve b--Excitation by the ultraviolet and the infrared light
 (PK-2 mercury lamp)

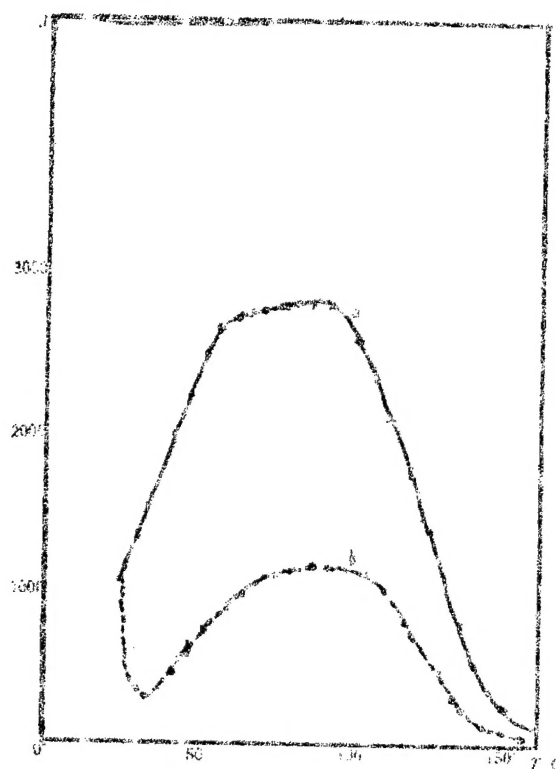
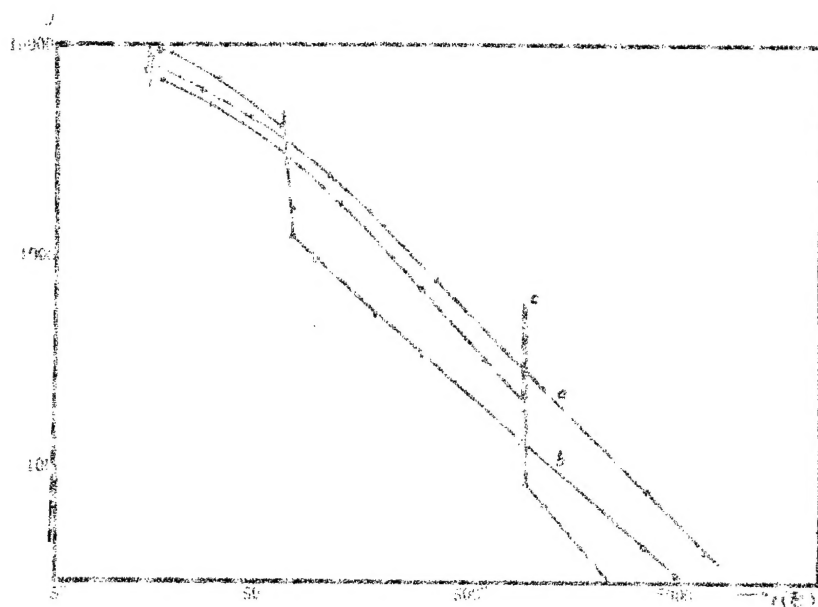


Figure 5 The Heat-Induced Light Curve of ZnS-Cu-Sm
 Curve a--After ultraviolet light excitation
 Curve b--10 seconds' infrared irradiation after ultraviolet
 excitation



second

Figure 6 The Effect of Infrared Light on the Rate of Decay of
Photoluminescence of ZnS-Cu-Sm
Curve a--After ultraviolet excitation
Curve b--10 seconds' infrared irradiation one minute after
ultraviolet excitation
Curve c--10 seconds' infrared irradiation 15 minutes after
ultraviolet excitation

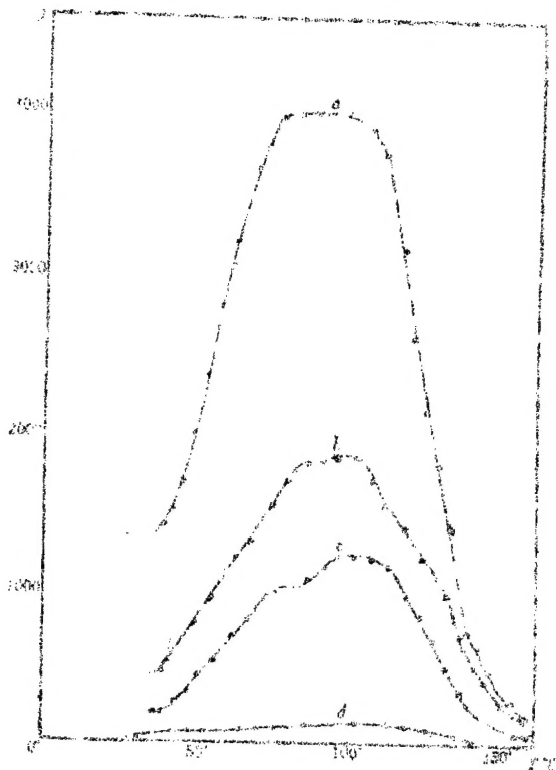


Figure 7 The Effect of Infrared Light on the Heat-Induced Light Curve of ZnS-Cu-Sm
 Curve a--Ultraviolet excitation without infrared irradiation
 Curve b--10 seconds' infrared irradiation after ultraviolet excitation
 Curve c--30 seconds' infrared irradiation after ultraviolet excitation
 Curve d--5 minutes' infrared irradiation after ultraviolet excitation

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